



Europäisches Patentamt
European Patent Office
Office européen des brevets



Publication number:

0 299 575 B1

12

EUROPEAN PATENT SPECIFICATION

45 Date of publication of patent specification: 12.01.94 61 Int. Cl.⁵: C11D 3/12, C11D 3/02

21 Application number: 88201455.8

22 Date of filing: 08.07.88

54 Detergent compositions.

30 Priority: 14.07.87 GB 8716584
29.09.87 GB 8722844
24.03.88 GB 8807012

43 Date of publication of application:
18.01.89 Bulletin 89/03

45 Publication of the grant of the patent:
12.01.94 Bulletin 94/02

84 Designated Contracting States:
AT BE CH DE FR GB GR IT LI LU NL SE

56 References cited:
EP-A- 0 137 669 EP-A- 0 150 531
EP-A- 0 240 057 EP-A- 0 242 918
FR-A- 2 568 888 GB-A- 1 384 244

73 Proprietor: THE PROCTER & GAMBLE COM-
PANY
One Procter & Gamble Plaza
Cincinnati Ohio 45202(US)

72 Inventor: Raemdonck, Hans
Belgielaan, 12
B-9820 St. Denijs Westrem(BE)
Inventor: Busch, Alfred
Luitberg, 10
B-1820 Strombeek-Bever(BE)

74 Representative: Canonici, Jean-Jacques et al
Procter & Gamble European Technical Cen-
ter N.V.
Temseleaan 100
B-1853 Strombeek-Bever (BE)

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

Rank Xerox (UK) Business Services
(3.10/3.9/3.3.3)

EP 0 299 575 B1

Description

The present invention relates to detergent compositions. More specifically it relates to detergent compositions containing a fabric-softening amount of a smectite-type clay. The compositions further contain a polymeric clay flocculating agent.

British Patent 1 400 898 discloses detergent compositions comprising, as a fabric-softening ingredient, a smectite-type clay. Any smectite-type clay having a cation exchange capacity of at least 50 meq/100 g is taught to be suitable. Gelwhite GP and Volclay BC, both of which are sodium montmorillonite clays, are disclosed to be preferred for reasons of color and cation exchange capacity.

It is now well recognized in the detergent industry that clays of the type disclosed in British Patent 1 400 898 provide significant fabric softening benefits when used in a laundry detergent. Yet, it is equally well recognized that deposition of these clays onto the fabrics during the laundering process is far from complete; in fact, under typical European laundry conditions, less than half of the available clay is deposited onto the fabrics, the remainder being rinsed away with the laundry liquor during the subsequent rinsing steps. Moreover, the softening effect obtained as a result of the clay deposition is affected by factors that are not well understood.

It is, therefore, an object of the present invention to provide detergent compositions comprising a fabric-softening clay from which the clay particles are more efficiently deposited onto fabrics during the laundry process. It is another object of the present invention to provide detergent compositions from which clay particles are efficiently deposited, regardless of the builder system used.

Summary of the Invention

The present invention relates to detergent compositions comprising from 5% to 40% of an organic surfactant and, as a fabric softening ingredient, from 1% to 30% of a smectite-type clay, characterized in that it further comprises a softening enhancing amount of a polymeric clay flocculating agent, in the range of from 0.005% to 20% by weight of the smectite-type clay.

Preferred clay flocculating agents are polymers like poly(ethylene oxide), poly(acryl amide) and poly(acrylate), having a weight average molecular weight of from 100.000 to 10 million, most preferably of from 150.000 to 5 million.

Detailed Description of the Invention

The detergent compositions of the present invention comprise conventional deterative surfactants, conventional detergent builders and, optionally, other conventional detergent ingredients. The compositions further comprise a fabric-softening amount, from 1% to 30% by weight of the detergent composition, of a fabric-softening clay.

Percentages herein are percentages by weight of the detergent compositions, unless otherwise specified.

The compositions further contain a polymeric clay-flocculating agent.

It has been found that polymeric clay-flocculating agents enhance the deposition of fabric-softening clays onto fabrics. The amount of clay-flocculating agent to be used in the present detergent compositions must be such that the deposition of the softening clay onto fabrics is enhanced, but remains substantially uniform. For a given polymeric clay-flocculating agent the amount required in the detergent composition can be readily determined in a simple level study using the clay deposition test described hereinbelow.

Clay deposition test

To samples of a detergent composition which contains 5% of a fabric-softening clay are added different levels of the polymeric clay-flocculating agent under investigation. Swatches of terry towel are laundered in 1% solutions of the respective detergent samples. The swatches are rinsed and line dried. The clay on the swatches is stained with methylene blue. The hue is compared to that obtained with a detergent sample to which no polymeric clay-flocculating agent has been added.

Any level of polymeric clay-flocculating agent that results in a hue that is perceptibly darker than that obtained without clay-flocculating agent gives the desired softness enhancing effect. Such level will be referred to herein as "a softness enhancing amount" of the clay-flocculating agent.

Relatively high levels of a clay-flocculating agent result in a patchy deposition or even reduced deposition of the clay. The stained swatches show blue spots, rather than a substantially uniform hue.

These relatively high levels of clay-flocculating agent do not result in the desired softness boost, and are therefore not considered softness enhancing amounts.

The amount of clay-flocculating agent, expressed as percent by weight of the smectite-type clay, ranges from 0.005 - 20% by weight of the clay, preferably from 0.05 - 20% by weight of the clay, for clay flocculating agents having a weight average molecular weight of from 150,000 to 800,000, and 0.005 to 2% by weight of the clay for MW 800,000 to 5 million.

Clay-flocculating agents are not commonly used in detergent compositions. On the contrary, one is inclined to use clay dispersants, which aid in removing clay stains from fabrics. Such agents are, however, very well known in other industries like oil well drilling, and for ore flotation in metallurgy. Most of these materials are fairly long chain polymers and copolymers derived from such monomers as ethylene oxide, acrylamide, acrylic acid, dimethylamino ethyl methacrylate, vinyl alcohol, vinyl pyrrolidone, ethylene imine. Gums, like guar gum, are suitable as well.

Preferred are polymers of ethylene oxide, acryl amide, or acrylic acid. For proper interaction with the clay particles, the polymers should be fairly long chain, i.e., have a weight average molecular weight of at least 100,000. For sufficient water-solubility the weight average molecular weight of the polymers should not exceed 10 million. Most preferred are polymers having a weight average molecular weight of from 150,000 to 5 million.

The fabric softening clay

Smectite-type clays are widely used as fabric softening ingredients in detergent compositions. Most of these clays have a cation exchange capacity of at least 50 meq/100g.

Montmorillonite clays are commonly used for this purpose. It appears, however, that certain hectorite clays provide better fabric softening performance than the more commonly used montmorillonites. The hectorites exhibiting this superior fabric softening performance are hectorites of natural origin.

The cation exchange capacity of clays is a well-known parameter and may be determined by well-established analytical techniques. See, for example, H. van Olphen, "Clay Colloid Chemistry", Interscience Publishers, 1963 and the relevant references cited therein.

Other detergent components

Detergent Surfactants - The compositions of this invention will typically contain organic surface-active agents ("surfactants") to provide the usual cleaning benefits associated with the use of such materials.

Detergent surfactants useful herein include well-known synthetic anionic, nonionic, amphoteric and zwitterionic surfactants. Typical of these are the alkyl benzene sulfonates, alkyl- and alkylether sulfates, paraffin sulfonates, olefin sulfonates, alkoxyated (especially ethoxyated) alcohols and alkyl phenols, amine oxides, alpha-sulfonates of fatty acids and of fatty acid esters, and the like, which are well-known from the detergency art. In general, such detergent surfactants contain an alkyl group in the C₉-C₁₈ range; the anionic detergent surfactants can be used in the form of their sodium, potassium or triethanolammonium salts; the nonionics generally contain from about 5 to about 17 ethylene oxide groups. U.S. Patent 3 995 669, contains detailed listings of such typical detergent surfactants. C₁₁-C₁₆ alkyl benzene sulfonates, C₁₂-C₁₈ paraffin-sulfonates and alkyl sulfates, and the ethoxyated alcohols and alkyl phenols are especially preferred in the compositions of the present type.

Also useful herein as the surfactant are the water-soluble soaps, e.g. the common sodium and potassium coconut or tallow soaps well-known in the art.

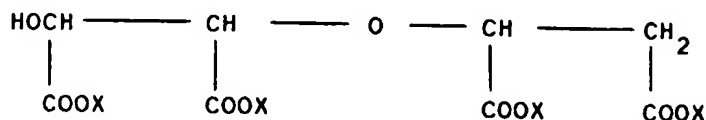
The surfactant component can comprise as little as 1% of the compositions herein, but preferably the compositions will contain 5% to 40%, preferably 10% to 30%, of surfactant. Mixtures of the ethoxyated nonionics with anionics such as the alkyl benzene sulfonates, alkyl sulfates and paraffin sulfonates are preferred for through-the-wash cleansing of a broad spectrum of soils and stains from fabrics. It has previously been disclosed that high levels of nonionic surfactants (i.e., in excess of 4%) in clay-containing detergent compositions negatively affect the clay softening performance. It has now surprisingly been found that such negative interaction does not occur if the clay flocculating agent of the present invention is also present.

Detergent Adjuncts - The composition herein can contain other ingredients which aid in their cleaning performance. For example, it is highly preferred that through-the-wash detergent compositions contain a detergent builder and/or metal ion sequestrant. Compounds classifiable and well-known in the art as detergent builders include the nitrilotriacetates, polycarboxylates, citrates, carbonates, zeolites, water-soluble phosphates such as tri-polyphosphate and sodium ortho- and pyro-phosphates, silicates, and

mixtures thereof. Metal ion sequestrants include all of the above, plus materials like ethylenediaminetetraacetate, the amino-polyphosphonates (DEQUEST®) and a wide variety of other poly-functional organic acids and salts too numerous to mention in detail here. See U.S. Patent 3 579 454 for typical examples of the use of such materials in various cleaning compositions. In general, the builder/sequestrant will comprise about 0.5% to 45% of the composition. The 1-10 micrometer size zeolite (e.g. zeolite A) builders disclosed in DE-A 2 422 655 are especially preferred for use in low-phosphate compositions.

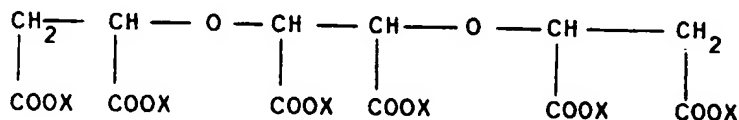
Particularly suitable phosphate-free builders are ether carboxylate mixtures comprising

a) from 1% to 99% of a tartrate monosuccinate component of the structure



wherein X is H or salt-forming cation; and

b) from 1% to 99% by weight of a tartrate disuccinate component of the structure :



wherein X is H or a salt-forming cation.

Builder systems of this type are more fully disclosed in U.S. patent N° 4,663,071, issued May 5, 1987 to Bush et al.

Typical detergent compositions contain from 5% to 35% of this builder system.

The laundry compositions herein also preferably contain enzymes to enhance their through-the-wash cleaning performance on a variety of soils and stains. Amylase and protease enzymes suitable for use in detergents are well-known in the art and in commercially available liquid and granular detergents. Commercial deterative enzymes (preferably a mixture of amylase and protease) are typically used at levels of 0.001% to 2%, and higher, in the present compositions. Detergent cellulase enzymes provide both cleaning and softening benefits, particularly to cotton fabrics. These enzymes are highly desirable in the detergent compositions of this invention.

The compositions herein can contain other ingredients which aid in their cleaning performance. For example, the compositions herein can advantageously contain a bleaching agent, especially a peroxyacid bleaching agent. In the context of the present invention, the term peroxyacid bleaching agent encompasses both peroxyacids per se and systems which are able to yield peroxyacids in situ.

Peroxyacids per se are meant to include the alkaline and alkaline-earth metal salts thereof. Peroxyacids and diperoxyacids are commonly used; examples are diperoxydodecanoic acid (DPDA) or peroxyphthalic acid.

Systems capable of delivering peracids in situ consist of a peroxygen bleaching agent and an activator thereof.

The peroxygen bleaching agents are those capable of yielding hydrogen peroxide in an aqueous solution; these compounds are well-known in the art, and include hydrogen peroxide, alkali-metal peroxides, organic peroxide bleaching agents such as urea peroxide, inorganic persalt bleaching agents such as alkali metal perborates, percarbonates, perphosphates, persulfates, and the like.

Preferred are sodium perborate, commercially available in the form of mono- and tetra-hydrates, sodium carbonate peroxyhydrate, sodium pyrophosphate peroxyhydrate and urea peroxyhydrate.

The liberated hydrogen peroxide reacts with a bleach activator to form the peroxyacid bleach. Classes of bleach activators include esters, imides, imidazoles, oximes, and carbonates. In these classes, preferred materials include methyl o-acetoxy benzoates; sodium-p-acetoxy benzene sulfonates such as sodium 4-

nonanoxyloxybenzene sulfonate; sodium-4-octanoxyloxybenzene sulfonate, and sodium-4-decanoxyloxybenzenesulfonate; bisphenol A diacetate; tetra acetyl ethylene diamine; tetra acetyl hexamethylene diamine; tetra acetyl methylene diamine.

Other highly preferred peroxygen bleach activators which are disclosed in U.S. Patents 4,483,778 and 4,539,130, are alpha-substituted alkyl or alkenyl esters, such as sodium-4-(2-chlorooctanoxyloxy)benzene sulfonate, sodium 4-(3,5,5-trimethyl hexanoxyloxy)benzene sulfonate. Suitable peroxyacids are also peroxygen bleach activators such as described in published European Patent Application N° 0 116 571, i.e., compounds of the general type RXAOOH and RXAL, wherein R is a hydrocarbyl group, X is a hetero-atom, A is a carbonyl bridging group and L is a leaving group, especially oxybenzenesulfonate.

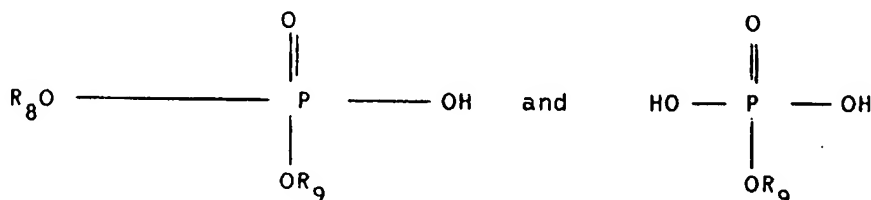
Other highly desirable detergent ingredients for use in the detergent compositions of the present invention are quaternary ammonium compounds of the formula $R_4 R_5 R_6 R_7 N^+ X^-$, wherein R_4 is alkyl having from 8 to 20, preferably from 12-18 carbon atoms, R_5 is alkyl having from 1 to 10 carbon atoms, and R_6 and R_7 are each C_1 to C_4 alkyl preferably methyl; X^- is an anion, e.g. chloride. Examples of such quaternary ammonium compounds include C_{12} - C_{14} alkyl trimethyl ammonium chloride and cocoalkyl trimethyl ammonium methosulfate. The quaternary ammonium compounds can be used at levels from 0.5% to 5%, preferably from 1% to 3%.

Additional softening ingredients

The detergent compositions of the present invention may further contain, in addition to the clay material, other softening ingredients. Suitable examples include amines of the formula $R_1 R_2 R_3 N$, wherein R_1 is C_6 to C_{20} hydrocarbyl, R_2 is C_1 to C_{20} hydrocarbyl, and R_3 is C_1 to C_{10} hydrocarbyl or hydrogen. A preferred amine of this type is ditallowmethylamine.

Preferably, the softening amine is present as a complex with a fatty acid of the formula $RCOOH$, wherein R is a C_8 to C_{20} alkyl or alkenyl. It is desirable that the amine/fatty acid complex be present in the form of microfine particles, having a particle size in the range of from, e.g., 0.1 to 20 micrometers. These amine/fatty acid complexes are disclosed more fully in European Patent Application N° 0 133 804. Preferred are compositions that contain from 1% to 10% of the amine.

Suitable are also complexes of the above described amine and phosphate esters of the formula



wherein R_8 and R_9 are C_1 - C_{20} alkyl, or ethoxylated alkyl groups of the general formula $\text{alkyl}-(\text{OCH}_2\text{CH}_2)_y$, wherein the alkyl substituent is C_1 - C_{20} , preferably C_8 - C_{16} , and y is an integer of 1 to 15, preferably 2-10, most preferably 2-5. Amine/phosphate ester complexes of this type are more fully disclosed in European Patent Application N° 0 168 889.

Further examples of optional softening ingredients include the softening amides of the formula $R_{10}R_{11}NCOR_{12}$, wherein R_{10} and R_{11} are independently selected from C_1 - C_{22} alkyl, alkenyl, hydroxy alkyl, aryl, and alkyl-aryl groups; R_{12} is hydrogen, or a C_1 - C_{22} alkyl or alkenyl, an aryl or alkyl-aryl group, or is $O-R_{13}$, wherein R_{13} is a C_1 - C_{22} alkyl or alkenyl, an aryl or alkyl-aryl group. Preferred examples of these amides are ditallow acetamide and ditallow benzamide. Good results are obtained when the amides are present in the composition in the form of a composite with a fatty acid or with a phosphate ester, as described hereinbefore for the softening amines.

The amides are present in the composition at 1%-10% by weight.

Suitable softening ingredients are also the amines disclosed in U.K. Patent Application GB 2 173 827, in particular the substituted cyclic amines disclosed therein. Suitable are imidazolines of the general formula 1-(higher alkyl) amido (lower alkyl)-2-(higher alkyl)imidazoline wherein higher alkyl is alkyl having from 12 to 22 carbon atoms, and lower alkyl is alkyl having from 1 to 4 carbon atoms.

A preferred cyclic amine is 1-tallowamidoethyl-2-tallowimidazoline. Preferred compositions contain from 1% to 10% of the substituted cyclic amine.

The amine and amide softening ingredients may be added as a dry powder to a detergent granule, or may be sprayed onto the detergent granule or onto a carrier, either in melted or in dissolved form. An example of a suitable carrier is perborate monohydrate.

Moreover, the compositions herein can contain, in addition to ingredients already mentioned, various other optional ingredients typically used in commercial products to provide aesthetic or additional product performance benefits. Typical ingredients include pH regulants, perfumes, dyes, bleach, optical brighteners, soil suspending agents, hydrotropes and gel-control agents, freeze-thaw stabilizers, bactericides, preservatives, suds control agents, bleach activators and the like.

In a through-the-wash mode, the compositions are typically used at a concentration of at least 400 ppm, preferably 0.05% to 1.5%, in an aqueous laundry bath at pH 7-11 to launder fabrics. The laundering can be carried out over the range from 5 °C to the boil, with excellent results.

INDUSTRIAL APPLICATION

The detergent compositions of the present invention can be formulated as granular or as liquid detergents. It has been found that clays having a high swelling capacity can be easily incorporated in a liquid detergent composition, while maintaining phase stability.

In preparing liquid detergent compositions the polymeric clay-flocculating agent can be mixed with the other detergent ingredients under stirring.

In preparing a granular detergent composition the polymeric clay-flocculating agent can be added in a variety of ways. It may be added to the crutcher mix prior to spray-drying; or it may be sprayed onto a granular detergent from solution in water or an organic solvent; or it may be dry-mixed, in the form of particles, with a granular detergent. The release of the flocculating agent can be controlled by incorporating it in a prill, or by microencapsulating it in a suitable microencapsulating agent.

In a preferred embodiment, agglomerates are formed of the fabric softening clay and the clay-flocculating agent. These agglomerates are dry mixed with the granular detergent composition.

The chemical stability of the clay-flocculating agent is improved by the addition of small amounts (typically from 0.05% to 1% by weight of the detergent composition) of a chelating agent. A preferred chelating agent is ethylenediamine tetramethylene phosphonic acid.

The clay-flocculating agent may also be incorporated in a detergent additive, e.g. in the form of a sheet or a pouch, that is to be added to the wash liquor on top of a conventional detergent composition. The laundry additive preferably also contains a fabric-softening clay and/or other fabric softening ingredients described hereinabove, so it may be used in conjunction with detergent compositions that themselves do not contain such a clay or such other softening ingredients.

In a very specific embodiment the polymeric clay-flocculating agent is formed into a water-soluble film. The film is formed into a pouch which is filled with a single dose of a clay-containing detergent composition. In use, the pouch will dissolve and release the detergent composition. The dissolved polymer will interact with the softening clay to enhance its deposition onto fabrics. Polymers of ethylene oxide are particularly suitable for use in this embodiment of the invention.

A fabric-softening clay and a softness enhancing amount of a polymeric clay-flocculating agent can also be incorporated into a rinse-added softener composition. Other softening agents, like quaternary ammonium compounds, may also be present.

EXAMPLES I -VII

The following granular detergent compositions are prepared :

	INGREDIENT	COMPOSITION							
		(% by weight)							
		I	II	III	IV	V	VI	VII	VIII
5									
10	C ₁₁₋₁₂ alkyl benzene sulfonate (Na)	7.0	5.0	4.0	1.0	6.5	20.1	6.7	7.0
	Tallow alcohol sulfate (Na)	-	2.0	-	-	1.0	-	-	-
	C ₁₄₋₁₅ alkyl sulfate (Na)	-	-	-	-	-	-	6.7	-
15	A-Olefin (C ₁₂₋₁₈) sulfonate (Na)	-	-	2.0	-	-	-	-	-
	Tallow alcohol ethoxylate (EO ₁₁)	1.0	2.0	2.0	-	0.8	-	-	1.0
	Fatty alcohol (C ₁₂₋₁₅)ethoxylate (EO ₇)	-	-	-	6.0	-	-	1.0	-
20	Hydrogenated Tallow fatty acid	2.5	1.0	-	1.0	1.0	-	-	2.5
	Coconut fatty acid	-	-	1.5	-	-	-	-	-
	Dodecyl trimethyl ammonium chloride	-	1.5	-	-	1.5	-	-	-
	Distearyl methyl amine	3.0	-	-	-	3.0	-	-	-
25	Ditallowbenzamide	-	4.0	-	-	-	-	-	3.0
	Dodecyl dimethyl ammonium N-Oxide	0.5	-	0.5	-	0.4	-	-	0.5
	Lauryl-N,N-dimethyl amine	-	-	2.5	-	-	-	-	-
	Sodium tripolyphosphate	24.0	18	22	32.0	-	36.9	26.3	24
30	Zeolite	-	-	-	-	20.0	-	-	-
	Polyethylene oxide (Mw=5MM)	0.05	-	-	-	0.05	0.1	0.1	-
	Polyethylene oxide (Mw=300M)	-	-	-	0.2	-	-	-	0.2
	Polyacrylate	-	0.2	-	-	-	-	-	-
35	Polyacrylamide	-	-	1.5	-	-	-	-	-
	1-tallow-amidoethyl-2-tallow-imidazoline	-	-	-	-	-	-	4.3	-
40									
45									
50									
55									

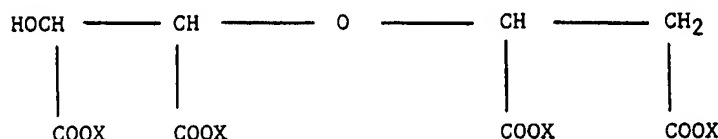
	INGREDIENT (% by weight)	COMPOSITION							
		(CONT'D)							
		I	II	III	IV	V	VI	VII	VIII
5	Sodium nitrilotriacetate	-	-	-	-	5.0	-	-	-
	Sodium sulfate	12.4	17.7	15.0	21.3	12.7	28.3	13.0	12.4
	Sodium carbonate	-	8.0	-	5.0	-	-	15.0	5
10	Sodium silicate	6.0	7.0	4.0	6.0	2.0	5.7	5.6	6.0
	Sodium perborate(4aq.)	20.0	15.0	18.0	10.0	18.0	-	5.0	15.0
	Carboxymethylcellulose	0.3	0.3	0.5	0.8	0.4	-	-	0.3
15	Polyacrylate (mw 1000-20000)	-	1.5	-	-	-	-	0.80	-
	Polyacrylate (mw 4000-5000)	-	-	-	-	3.0	-	-	-
	Copolymer maleic acid/acrylic acid (70/30) (mw 40.000-80.000)	2.0	-	1.5	2.5	-	-	-	2.0
20	Enzymes (protease, amylase, cellulase)	0.6	0.2	0.5	0.5	0.3	-	0.6	0.6
	Optical brightener	0.2	0.2	0.3	0.3	0.25	-	0.8	0.2
	Sulphonated zinc phthalocyanine	30ppm	-	-	25ppm	25ppm	-	-	30ppm
	EDTA	0.2	0.2	0.3	0.15	0.2	-	0.1	0.2
25	Ethylenediamine tetramethylene phosphonic acid	0.2	0.1	-	0.1	0.1	-	-	0.2
	Tetraacetyl ethylenediamine	1.5	-	-	-	1.5	-	-	2.0
	Iso-nonanoyloxy-benzene sulfonate (Na)	-	2.0	-	-	-	-	2.0	-
30	Silicone/silica suds suppressor	0.2	0.15	0.15	0.25	0.2	-	0.30	0.2
	Perfume	0.25	0.25	0.30	0.2	0.25	0.2	0.25	0.25
	Montmorillonite clay	10.0	7.0	15.0	5.0	10.0	-	5.6	9.5
	Hectorite clay	-	-	-	-	-	8.9	-	-
35	Moisture and minors	- balance to 100 -							

Claims

1. A detergent composition comprising from 5% to 40% of an organic surfactant, and as a fabric softening ingredient, from 1% to 30% of a smectite type clay, characterized in that said composition comprises a softness enhancing amount of a polymeric clay-flocculating agent in the range of from 0.005% to 20% by weight of the smectite type clay.
2. A detergent composition according to claim 1 wherein the clay flocculating agent is a polymer or a copolymer derived from monomers selected from ethylene oxide, acryl amide, acrylic acid, dimethylamino ethyl methacrylate, vinyl alcohol, vinyl pyrrolidone, ethylene imine, and mixtures thereof; said polymer having a weight average molecular weight of from 100.000 to 10 million.
3. A detergent composition according to claim 2 wherein the polymer is derived from monomers selected from ethylene oxide, acryl amide, and acrylic acid.
4. A detergent composition according to any one of the preceding claims wherein the polymeric clay flocculating agent has a weight average molecular weight of from 150.000 to 5 million.
5. A detergent composition according to any one of the preceding claims wherein the clay flocculating agent has a molecular weight of from 150.000 to 800.000 and is present in an amount of from 0.05 to

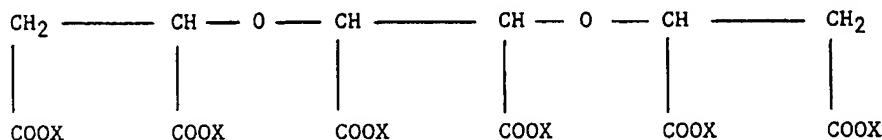
20% by weight of the smectite-type clay.

6. A detergent composition according to any one of claims 1-4 wherein the clay flocculating agent has a molecular weight of from 800.000 to 5 million and is present in an amount of from 0.005 to 2% by weight of the smectite-type clay.
7. A detergent composition according to any one of the preceding claims, further comprising from 0.5% to 5% of a quaternary ammonium compound of the formula $R_4R_5R_6R_7N^+X^-$, wherein R_4 is alkyl having from 10 to 20 carbon atoms, R_5 , R_6 and R_7 are each C_1 to C_4 alkyl, and X^- is an anion.
8. A detergent composition according to any one of the preceding claims further comprising from 1% to 10% of an amide of the formula $R_{10}R_{11}NCOR_{12}$, wherein R_{10} and R_{11} are independently selected from C_1 - C_{22} alkyl, alkenyl, hydroxy alkyl, aryl, and alkyl-aryl groups; R_{12} is hydrogen, or a C_1 - C_{22} alkyl or alkenyl, aryl or alkyl-aryl group, or is $O-R_{13}$, wherein R_{13} is a C_1 - C_{22} alkyl or alkenyl, an aryl or alkyl-aryl group.
9. A detergent composition according to any of the preceding claims, further comprising from 1% to 10% of an imidazoline of the formula 1-(higher alkyl) amido(lower alkyl)-2-(higher alkyl)imidazoline wherein higher alkyl is alkyl having from 12 to 22 carbon atoms, and lower alkyl is alkyl having from 1 to 4 carbon atoms.
10. A detergent composition according to any one of the preceding claims, further comprising from 5% to 35% of a builder system, said builder system comprising
 - a) from 1% to 99% of a tartrate monosuccinate component of the structure :



wherein X is H or a salt-forming cation; and

b) from 1% to 99% by weight of a tartrate disuccinate component of a structure.



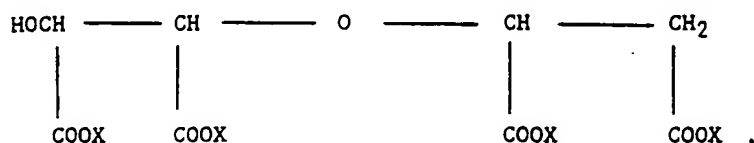
wherein X is H or a salt-forming cation

11. A laundry additive comprising a softener enhancing amount of a polymeric clay-flocculating agent, said additive being in the form of a pouch or a film-forming a pouch filled with a single dose of clay-containing detergent compositions.
12. A laundry additive according to claim 11, further comprising a fabric softening clay and/or other fabric softening ingredients.
13. A rinse-added softener comprising from 1% to 30% of a smectite type clay and a softness enhancing amount of a polymeric clay-flocculating agent in the range of 0.005% to 20% by weight of the smectite type clay.

14. A rinse-added softener according to claim 13 further comprising a fabric softener and/or other fabric softening ingredients.

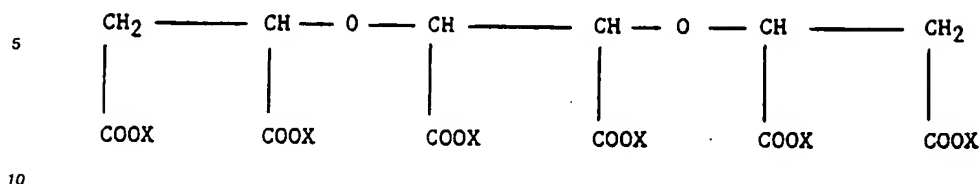
Patentansprüche

1. Detergengenzusammensetzung, umfassend 5% bis 40% eines organischen grenzflächenaktiven Mittels, und als einen gewebeweichmachenden Bestandteil 1% bis 30% eines Smectit-artigen Tones, dadurch gekennzeichnet, daß die genannte Zusammensetzung eine die Weichheit erhöhende Menge eines polymeren Tonflockungsmittels im Bereich von 0,005 Gew.-% bis 20 Gew.-% des Smectitartigen Tones umfaßt.
2. Detergengenzusammensetzung nach Anspruch 1, worin das Tonflockungsmittel ein Polymer oder ein Copolymer ist, welches sich aus Monomeren herleitet, die unter Ethylenoxid, Acrylamid, Acrylsäure, Dimethylaminoethylmethacrylat, Vinylalkohol, Vinylpyrrolidon, Ethylenimin und Gemischen hievon ausgewählt sind; welches Polymer ein Gewichtsmittel-Molekulargewicht von 100.000 bis 10 Millionen besitzt.
3. Detergengenzusammensetzung nach Anspruch 2, worin das Polymer aus Monomeren erhalten wird, welche unter Ethylenoxid, Acrylamid und Acrylsäure ausgewählt sind.
4. Detergengenzusammensetzung nach einem der vorstehenden Ansprüche, worin das polymere Tonflockungsmittel ein Gewichtsmittel-Molekulargewicht von 150.000 bis 5 Millionen aufweist.
5. Detergengenzusammensetzung nach einem der vorstehenden Ansprüche, worin das Tonflockungsmittel ein Molekulargewicht von 150.000 bis 800.000 besitzt und in einer Menge von 0,05 Gew.-% bis 20 Gew.-% des Smectit-artigen Tones vorliegt.
6. Detergengenzusammensetzung nach einem der Ansprüche 1 bis 4, worin das Tonflockungsmittel ein Molekulargewicht von 800.000 bis 5 Millionen besitzt und in einer Menge von 0,005 Gew.-% bis 2 Gew.-% des Smectit-artigen Tones vorliegt.
7. Detergengenzusammensetzung nach einem der vorstehenden Ansprüche, welche ferner 0,5 % bis 5 % einer quaternären Ammoniumverbindung der Formel $R_4 R_5 R_6 R_7 N^+ X^-$ enthält, worin R_4 Alkyl mit 10 bis 20 Kohlenstoffatomen ist, R_5 , R_6 und R_7 jeweils C_1 - C_4 -Alkyl darstellen und X^- ein Anion bedeutet.
8. Detergengenzusammensetzung nach einem der vorstehenden Ansprüche, welche ferner 1% bis 10% eines Amides der Formel $R_{10} R_{11} NCOR_{12}$ enthält, worin R_{10} und R_{11} unabhängig voneinander unter C_1 - C_{22} -Alkyl-, -Alkenyl-, -Hydroxyalkyl-, Aryl- und Alkylarylgruppen ausgewählt sind; R_{12} für Wasserstoff oder eine C_1 - C_{22} -Alkyl- oder -Alkenyl-, Aryl- oder Alkylarylgruppe steht, oder $O-R_{13}$ darstellt, worin R_{13} eine C_1 - C_{22} -Alkyl- oder -Alkenyl-, eine Aryl- oder Alkylarylgruppe bedeutet.
9. Detergengenzusammensetzung nach einem der vorstehenden Ansprüche, welche ferner 1% bis 10% eines Imidazolins der Formel 1-(Höheralkyl)amido(niederalkyl)-2-(höheralkyl)imidazolin enthält, worin Höheralkyl für Alkyl mit 12 bis 22 Kohlenstoffatomen steht und Niederalkyl Alkyl mit 1 bis 4 Kohlenstoffatomen ist.
10. Detergengenzusammensetzung nach einem der vorstehenden Ansprüche, welche ferner 5% bis 35% eines Gerüststoffsystems umfaßt, welches Gerüststoffsystem
 - a) 1% bis 99% einer Tartratmonosuccinatkomponente der Struktur:



worin X für H oder ein salzbildendes Kation steht; und

b) 1 Gew.-% bis 99 Gew.-% einer Tartratdisuccinatkomponente der Struktur:



enthält, worin X für H oder ein salzbildendes Kation steht.

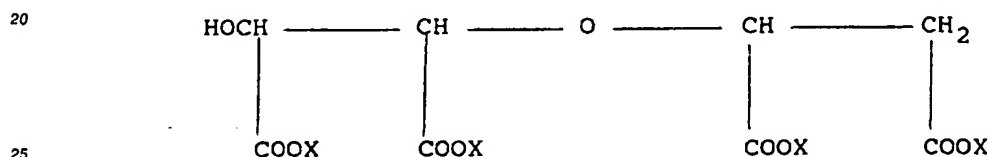
11. Wäschewaschzusatz, umfassend eine die Weichheit erhöhende Menge eines polymeren Tonflockungsmittels, welcher Zusatz in der Form eines Beutels oder einer einen Beutel ausbildenden Folie vorliegt, welcher Beutel mit einer einfachen Dosis der Ton-enthaltenden Detergensenzusammensetzungen befüllt ist.
12. Wäschewaschzusatz nach Anspruch 11, welcher ferner einen gewebeweichmachenden Ton und/oder andere gewebeweichmachende Bestandteile umfaßt.
13. Weichmacher, welcher beim Spülen zugesetzt wird, umfassend 1% bis 30% eines Smectit-artigen Tones und eine die Weichheit erhöhende Menge eines polymeren Tonflockungsmittels im Bereich von 0,005 Gew.-% bis 20 Gew.-% des Smectit-artigen Tones.
14. Weichmacher, welcher beim Spülen zugesetzt wird, nach Anspruch 13, welcher ferner einen Gewebeweichmacher und/oder andere gewebeweichmachende Bestandteile umfaßt.

Revendications

1. Composition détergente comprenant 5 à 40 % d'un agent tensio-actif organique et, à titre d'ingrédient d'adoucissement des tissus, 1 à 30 % d'une argile de type smectite, caractérisée en ce que ladite composition comprend une quantité d'un agent polymère de flocculation de l'argile favorisant l'adoucissement à raison de 0,005 à 20 % en poids de l'argile de type smectite.
2. Composition détergente selon la revendication 1, dans laquelle l'agent de flocculation de l'argile est un polymère ou un copolymère dérivé de monomères choisis parmi l'oxyde d'éthylène, les acrylamides, l'acide acrylique, les diméthylamino éthyl méthacrylates, les alcools vinyliques, la vinyl pyrrolidone, les éthylène imines et leurs mélanges, ledit polymère ayant un poids moléculaire moyen en poids de 100.000 à 10.000.000.
3. Composition détergente selon la revendication 2, dans laquelle le polymère est dérivé de monomères choisis parmi l'oxyde d'éthylène, les acrylamides et l'acide acrylique.
4. Composition détergente selon l'une quelconque des revendications précédentes, dans laquelle l'agent polymère de flocculation de l'argile a un poids moléculaire moyen en poids de 150.000 à 5.000.000.
5. Composition détergente selon l'une quelconque des revendications précédentes, dans laquelle l'agent de flocculation de l'argile a un poids moléculaire de 150.000 à 800.000 et est présent à raison de 0,05 à 20 % en poids de l'argile de type smectite.
6. Composition détergente selon l'une quelconque des revendications 1 à 4, dans laquelle l'agent de flocculation de l'argile a un poids moléculaire de 800.000 à 5.000.000 et est présent à raison de 0,005 à 2 % en poids de l'argile de type smectite.
7. Composition détergente selon l'une quelconque des revendications précédentes, comprenant par ailleurs 0,5 à 5 % d'un composé d'ammonium quaternaire de formule $R_4 R_5 R_6 R_7 N^+ X^-$ dans laquelle R_4 est un groupe alkyle ayant 10 à 20 atomes de carbone, R_5 , R_6 et R_7 sont chacun un groupe alkyle en

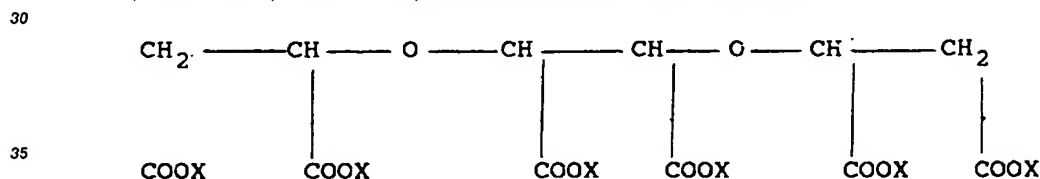
C₁ à C₄ et X⁻ est un anion.

8. Composition détergente selon l'une quelconque des revendications précédentes, comprenant par ailleurs 1 à 10 % d'un amide de formule R₁₀R₁₁NCOR₁₂, dans laquelle R₁₀ et R₁₁ sont indépendamment choisis parmi un groupe alkyle en C₁-C₂₂, un groupe alcényle, un groupe hydroxy alkyle, un groupe aryle et un groupe alkylaryle, R₁₂ est de l'hydrogène ou un groupe alkyle ou alcényle en C₁-C₂₂, un groupe aryle ou alkylaryle ou un groupe O-R₁₃, dans lequel R₁₃ est un groupe alkyle ou alcényle en C₁-C₂₂, ou bien un groupe aryle ou alkylaryle.
9. Composition détergente selon l'une quelconque des revendications précédentes, comprenant par ailleurs 1 à 10 % d'une imidazoline de formule 1-(alkyle supérieur) amido (alkyle inférieur) -2-(alkyle supérieur) imidazoline dans laquelle le groupe alkyle supérieur est un groupe alkyle ayant 12 à 22 atomes de carbone et le groupe alkyle inférieur est un groupe alkyle ayant 1 à 4 atomes de carbone.
10. Composition détergente selon l'une quelconque des revendications précédentes, comprenant par ailleurs 5 à 35 % d'un système d'adjuvants, ledit système d'adjuvants comprenant :
- a) 1 à 99 % d'un composant de tartrate monosuccinate de structure :



dans laquelle X est de l'hydrogène ou un cation formateur de sel, et

b) 1 à 99 % en poids d'un composant de tartrate disuccinate de structure :



dans laquelle X est de l'hydrogène ou un cation formateur de sel.

11. Additif de blanchisserie contenant une quantité d'un agent polymère de flocculation de l'argile favorisant l'adoucissement, ledit additif se présentant sous la forme d'un sachet ou d'un film formant un sachet rempli d'une dose unique de composition détergente contenant de l'argile.
12. Additif de blanchisserie selon la revendication 11, comprenant par ailleurs une argile d'adoucissement des tissus et/ou d'autres ingrédients d'adoucissement des tissus.
13. Adoucisseur ajouté à l'eau de rinçage et comprenant 1 à 30 % d'une argile de type smectite et une quantité d'un agent polymère de flocculation de l'argile favorisant l'adoucissement en quantité de 0,005 à 20 % en poids de l'argile de type smectite.
14. Adoucisseur ajouté à l'eau de rinçage selon la revendication 13 comprenant par ailleurs un adoucisseur de tissu et/ou d'autres ingrédients d'adoucissement des tissus.